1969

The Vapor-Liquid and Liquid-Liquid Phase Equilibria for the Partially Miscible System Methanol-Cyclohexane

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THE VAPOR-LIQUID AND LIQUID-LIQUID PHASE EQUILIBRIA FOR THE PARTIALLY MISCIBLE SYSTEM METHANOL-CYCLOHEXANE

(TITLE)

BY

RICHARD A. CHRISTMAN

B.S., Eastern Illinois University, 1968

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1969
YEAR

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ACKNOWLEDGMENTS

The author would like to express his gratitude to Dr. George L. Cunningham, Jr. for his direction and encouragement during this research project.

I would like to thank the members of my committee for their help and interest in the progress of this investigation. I would also like to express my appreciation to the entire chemistry department faculty for their invaluable guidance over the past years.

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ABSTRACT

By use of techniques of previous workers for determining liquid-liquid equilibrium and through the use of a circulation still, the complete phase diagram for the partially miscible system, methanol-cyclohexane, was determined. The accuracy of earlier liquid-liquid phase data was not improved upon although it was closely approximated. The critical solution temperature was found to be 46.4 degrees C., which is within the range of temperatures reported in earlier measurements.

Activity coefficients of methanol and cyclohexane were calculated from the phase boundaries of the boiling point diagram determined in the present investigation. These activity coefficients were in agreement with the Gibbs-Duhem equation and with the theoretically predicted activity coefficients of the van Laar and Margules equations. Vapor-liquid phase data previously available was limited to the azeotrope boiling temperature reported to be 54.2 degrees C.

INTRODUCTION

Although the experimental data for a complete boiling point diagram for methanol and cyclohexane has not previously been determined, the liquid-liquid phase data has been determined by several independent researchers.[10] The first of such measurements was made by Lecat in 1909 and tabulations may be found in the International Critical Tables.[6] Thus far the most accurate data has been determined by E. L. Eckfeldt and W. W. Lucasse.[3] The method used in the present experiment closely parallels the experimental technique of Eckfeldt and Lucasse which is considered one of the most accurate methods available for measuring liquid-liquid phase equilibrium. Their technique outlined briefly is as follows: the two components were measured into ampoules which were sealed and transferred to a variable temperature water bath where phase changes were observed at the saturation temperature. Earlier workers also measured the effects of added substances on the miscibility temperatures of the system.

Data for the vapor-liquid phase equilibrium of partially miscible liquids is also necessary and in many cases is more difficult to measure than the liquid-liquid phase boundary. "In view of the growing importance of industrial distillation systems involving the miscible region of partially miscible liquids, an adequate method of measuring the vapor-liquid equilibrium of

such systems is greatly to be desired."[2]

There are five standard methods for the direct determination of vapor-liquid equilibrium: distillation method, circulation method, static method, dew and bubble point method, and flow method.[4] The present investigation incorporated the circulation method because of its availability, ease of operation, and thermodynamically consistent results.

The flow method, which was used by A. P. Colburn, E. M. Schoenborn, and David Shilling in 1943 to gather data on the system isobutanol-water, is perhaps the most sophisticated technique available.[2] In their measurements they employed the Colburn flow still in which the vapors of the pure components are each introduced at a constant and controlled rate into the liquid. If condensation or evaporation occurs in the liquid, the system is not at equilibrium. When the volume of the liquid becomes constant, the system is assumed to be at the equilibrium temperature. The liquid is then sampled and analyzed. The vapor concentration is determined by the ratio of the flow rates. This system gives good results but demonstrates certain operational difficulties.

In addition to the flow still some circulation stills have met requirements for use with partially miscible systems. One of these circulation stills is the Thornton still.[4] The special feature of this unit is that the receiver for collecting condensate is located directly in the vapor space. This prevents the condensate from separating into two phases. A second circula-

tion still which proved satisfactory was the circulation still used by Smith and Bonner.[9] Its unique feature was also in the design of the receiver which is mounted externally.

Determination of the vapor-liquid equilibrium data permits the preparation of a more complete phase diagram which indicates more clearly the state of the system at a given temperature and composition. The activity coefficients of each component, which are derived from vapor-liquid phase data, describe the interactions between the individual molecules of each component at various concentrations. The purpose of the present investigation is to provide a more exact diagram for cyclohexane and methanol than theoretically predicted, and to calculate the activity coefficients of each component.

EXPERIMENTAL

LIQUID-LIQUID PHASE DATA

Apparatus

The ampoules which were used had an average volume of one and one half milliliters and were drawn from four-inch, soft glass test tubes. The average ampoule was ten centimeters long and the narrow stem was wide enough to allow the insertion of a stainless steel needle fitted to a surgical syringe used in filling the ampoules. An Ainsworth balance (type 10) with a precision of 0.1 milligram was used for weight determination. Small vials with rubber septum stoppers were used to contain methanol.

A 1000 milliliter beaker served as a water bath and allowed the ampoule to be viewed from all angles. It was fitted with an immersion heater made from glass rod bent into a large circle, which fit at the bottom of the beaker. The circular rod was wound with Nicrome high-resistance wire. The current to the heater was controlled by a variable output transformer. A water-turbine magnetic stirrer was more suited for the present purpose since electric stirrers produce unwanted heat. Measurements of temperature were made with a Kimble 76 mm. #596 immersion thermometer having division every 0.1 degree C. In order to reach ampoule temperatures below that of the room and

to gain more control over the rate of cooling, the beaker was partially submerged into a polyethylene dish which acted as an ice bath. The dish was fitted with a vacuum tubing which drew off melted ice as fresh ice was added, eliminating the necessity of stopping to empty the ice bath during measurement procedures. This apparatus permitted precise temperature control of the water bath in the beaker.

An incandescent lamp mounted just above and to the left of the beaker provided good illumination necessary to detect subtle miscibility changes of the components in the ampoule. During observation the ampoule was held near the highly reflective bulb of the thermometer which assisted in illuminating the ampoule and reduced the chance of any thermometer-ampoule temperature gradients. Each ampoule was secured by its stem using a modified wooden test-tube holder to allow each ampoule to be agitated vigorously. Vigorous agitation was necessary to insure thorough mixing. The securing device used reduced the chances of breakage.

Procedure

Due to the hygroscopic nature of the alcohol,[7] it was necessary to minimize its contact with the atmosphere. The absolute alcohol was transferred immediately from its original container to the small glass vials with septums. The soft rubber septums allowed the alcohol to be drawn into a syringe with minimal atmospheric contact. These vials were not suitable to contain cyclohexane since this component quickly decomposed the rubber

septum. Different stoppers of various compositions were tested but none were found to be suitable for use with cyclohexane. This problem was left unsolved since cyclohexane is not as hygroscopic as methanol. The C. P. cyclohexane was transferred to a small screw stoppered bottle which was only opened in a dehumidified room during filling of ampoules.

The method of filling and sealing the ampoules was similar to that used by Jones and Amstell.[7] Filling of the ampoules was accomplished by using a separate syringe for each component. The stem of the empty ampoule was first fitted with a short section of thin rubber tubing that was closed at one end and allowed the ampoule to be temporarily sealed. The ampoule was then reweighed to 0.1 milligram. Cyclohexane was injected with the first syringe and the ampoule was temporarily sealed and reweighed. Methanol was then injected with the second syringe after which the ampoule was resealed and reweighed. The ampoule was then partially submerged into a salt-water ice bath. Enough time was allowed for complete cooling to lower the vapor pressure of the contents. While still in the ice bath the stem of the ampoule was permanently sealed off with a small hot flame from an air-gas torch. When filling, care was taken to prevent wetting the sides of the ampoules since these traces would produce unwanted moisture if ignited while sealing. There were eleven ampoules filled having various mole fractions of methanol ranging from 0.1197 to 0.9274.

Results

The miscibility behavior of the components at the saturation temperature varied depending on the mole fraction of methanol in the ampoule under observation. The ampoules with mole fractions ranging from approximately 0.30 to 0.60 had a saturation temperature near the critical solution temperature. In this concentration range the behavior exhibited by the system in going from one to two phases was as follows: at a temperature within a degree above the phase transition, the solution was clear with no trace of color or dispersion; as the temperature was lowered approaching the saturation point, an incipient region occurred where the color gradually became bluish and opalescent, yet was still translucent. At the phase transition, within a temperature range of ±0.05 degrees C., the system suddenly became opaque, and the blue color was no longer present. In observing ampoules with components having mole fractions in a region less than 0.30 and greater than 0.60, the incipient region was found to be identified by a fine but visible dispersion of the particles which did not display blue opalescence. The transition from the translucent dispersion to opaqueness was as sharp as it was in the region of the critical solution temperature. There was a slight difference in temperature between the point of clearing and the point of clouding. To prevent error due to the possibility of metastability, the points of clouding were chosen as the saturation temperature.[3]

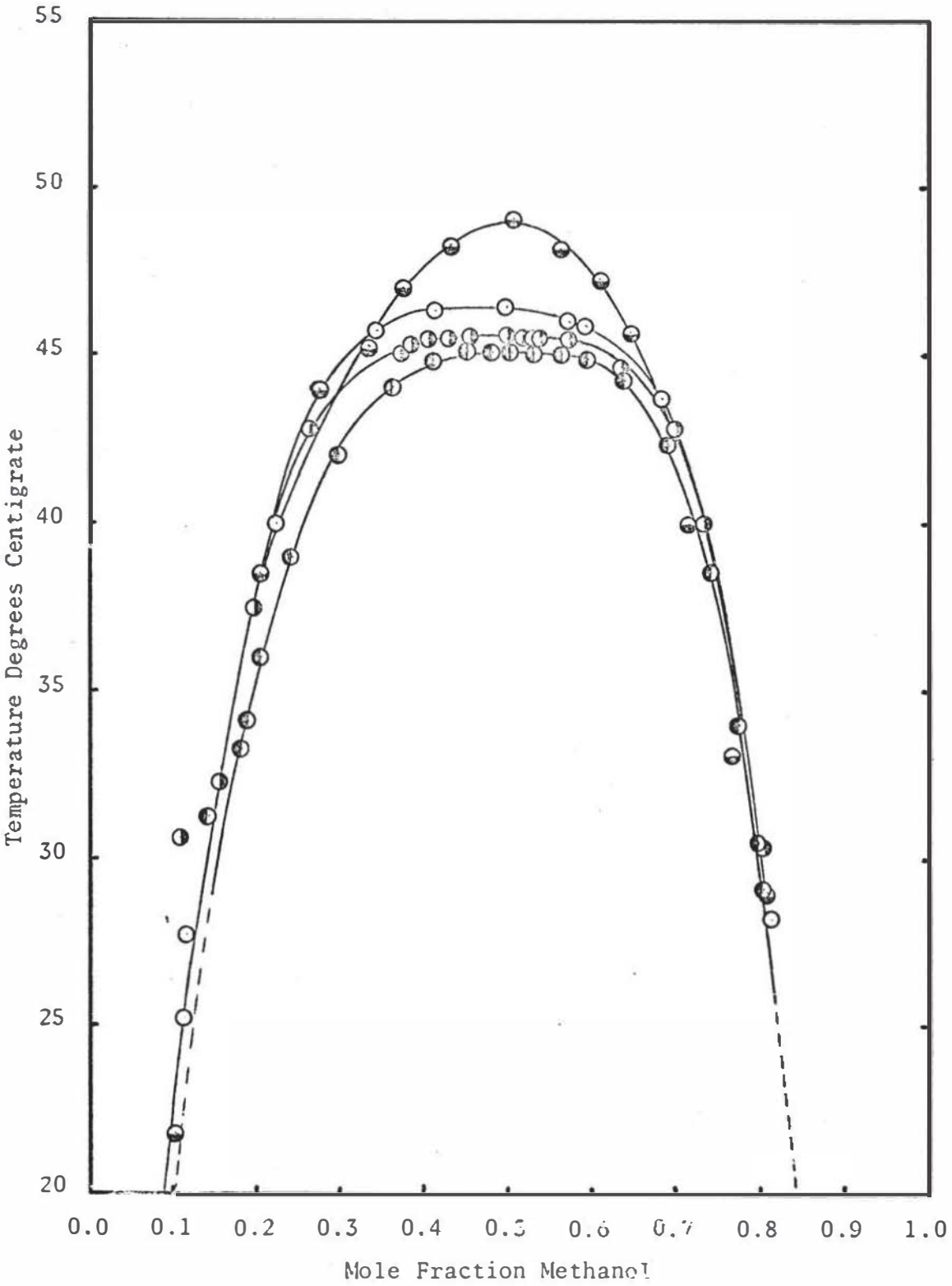
Table 1.

Experimental Liquid-Liquid Equilibrium Data for System, Methanol-Cyclohexane.

Ampoule No.	Weight Fraction Methanol	Mole Fraction Methanol	Saturation Temperature
1	0.0465	0.1135	25.2
2	0.0492	0.1197	27.6
3	0.0995	0.2249	40.0
4	0.1698	0.3425	45.7
5	0.2121	0.4142	46.3
6	0.2762	0.5006	46.4
7	0.3382	0.5731	46.0
8	0.3582	0.5945	45.8
9	0.4520	0.6842	43.7
10	0.6247	0.8156	28.2

Figure 1

Liquid-Liquid Equilibrium for System Methanol-Cyclohexane



VAPOR-LIQUID PHASE DATA

Apparatus

The Choppin-Cottrell circulation still, made by Sargent-Welch Scientific Co. (Item S-62000), was used in the present experiment. It consisted essentially of a cylindrical boiling flask which held approximately 30 milliliters of liquid, a Cottrell pump, and a reflux condenser. Temperature measurements were made with a Kimble 76 mm. #S96 immersion thermometer having division every 0.1 degree C. The large Cottrell pump reduced superheating by directing slugs of the liquid in equilibrium with the vapor onto the bulb of the thermometer. The vapor tube which surrounded the thermometer and the Cottrell pump also helped reduce superheating by separating the space in which the temperature is measured from that where the liquid is brought to a boil. Heat was supplied by a standard Bunsen burner used in conjunction with an asbestos plate located under the boiling flask with a center hole which exposed only a small bottom portion of the flask. This plate also served to help prevent superheating.

A medium sized reflux condenser directed the condensate to the return line which also acted as the receiver. At the base of the return line was a three-position stopcock. One position of the stopcock allowed boiling to reach equilibrium by returning the condensate directly to the base of the boiling flask. Another position allowed the condensate to be sampled, and a third position allowed the distillate to be sampled. The samples were collected in small screw-stoppered bottles having

aluminum foil liners that were not affected by the components. These bottles also served in the preparation of the standard samples used in analysis.

Purification of Chemicals

Absolute methanol and C. P. cyclohexane (Eastman Organic Chemicals) were used. They were purified in an 80 centimeter vacuum-jacketed fractionating column packed with Berl saddles. A reflux ratio of about one to five was used.

Procedure

For every run made there were two samples taken, one of distillate and one of condensate. Each series of runs began by having a pure component in the flask and heating it long enough to establish a steady boiling temperature indicating that equilibrium was reached. At this point the boiling temperature was recorded and the system was allowed to cool. A small portion of the second component was added to the boiling flask and the system was again heated until equilibrium was attained. The temperature was then recorded. The stopcock was turned to a closed position and the heat was removed. A sample of the condensate was taken immediately while the receiver was still hot. Directly afterwards the distillate sample was taken. The still was then allowed to cool after which time an additional portion of the second component was added and the system was again heated until equilibrium was reached. A series of such runs was made until the azeotrope temperature was reached or passed, at which time the still was cleaned. Then starting

with a pure second component, a second series of runs was made. In the present analysis there were four such series of runs made on three separate days with a total of thirty separate runs in all. Since the Choppin-Cottrell still is an open system, it was found necessary to record the barometric pressure prior to each series of runs.

Sample Analysis

The samples were analysed using quantitative vapor phase chromatographic techniques. Since the samples were heterogeneous at room temperature in all but the very dilute regions, it was found necessary to make them homogenous. Toluene was used for this purpose since both components were mutually miscible in it. The toluene was added to both the standard and the unknown samples in equal volume to weight ratios of one milliliter toluene to one milligram of sample. The toluene was delivered to each sample in a one milliliter blow-out pipet. Weight measurements of both samples and standards were made on an Ainsworth (type 10) balance which weighed to 0.1 milligram. All sample bottles were weighed before and after each run.

In the present experiment, peak height rather than peak area was used as the measurement to be related to sample mole fraction. For this reason, the conditions of the gas chromatograph were adjusted to minimum allowable peak separation with a maximum peak height. These conditions were established on a Carle Basic gas chromatograph using a Heath servo-recorder model EUW-20A. A dinonylphthalate column was used since it

gave three clean separations: methanol, cyclohexane, and toluene with retention times of 25, 38, and 85 seconds respectively. The inlet temperature was set at 122 degrees C., the column temperature at 112 degrees C. The flow rate using helium as a carrier gas was 18 milliliters per minute. Sample volumes were two microliters and the attenuation was set at five. Microsep F-138 septums which had a film of teflon on one side making them more suited for work at higher temperatures were used since it was found that they did not leak as did the conventional septums. It was necessary that no leakage occurred since all variables were to be held constant throughout the present investigation.

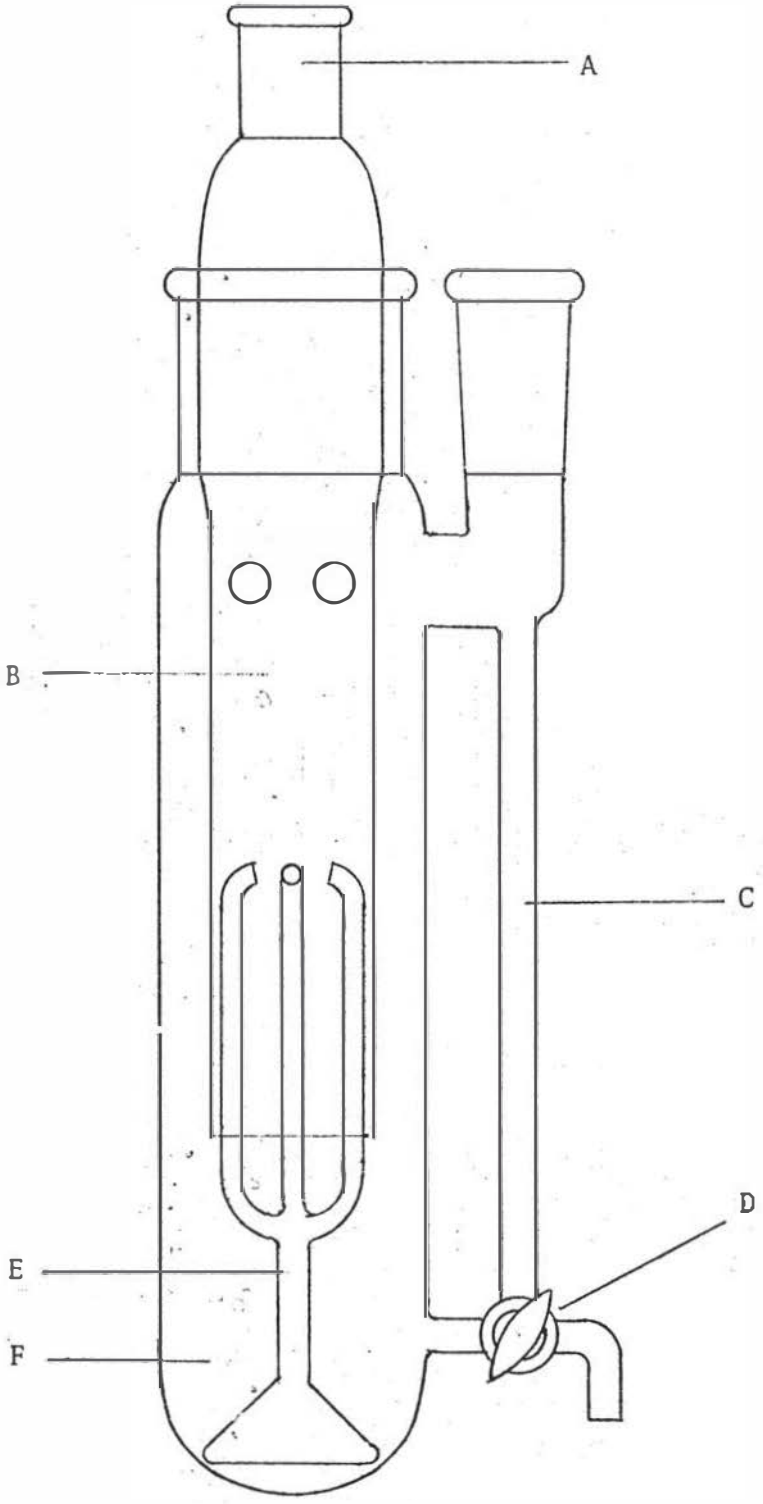
The peak fraction, i.e. the methanol peak height divided by the sum of the peak height of methanol and cyclohexane, was used as opposed to the originally proposed peak ratio. The peak fraction gave a relatively straight line relationship when plotted against the mole fraction. The peak ratio did not do so. It was also found that the concentration of toluene affected the ratio. Its percentage for this reason was held constant.

Four injections of each sample were made on the average, with the mean peak percentage chosen as representative of that sample. Ten standards, which ranged in mole fraction from 0.1193 to 0.9078 were always run during the same period of analysis as were the samples to which they were compared. There were two sets of ten standards prepared and run at

different periods of analysis. Both sets gave equivalent standardization curves.

Figure 2

Choppin-Cottrell Circulation Still



A - Thermometer Neck

B - Vapor Tube

C - Receiver

D - 3-position Stopcock

E - Cottrell Pump

F - Boiling Flask

(Thermometer and Reflux Condenser not shown)

Table 2.

Experimental Data for Standard Samples.

Sample No.	Mole Fraction Methanol	Peak % Methanol
1	0.119	0.123
2	0.195	0.198
3	0.228	0.296
4	0.370	0.351
5	0.469	0.425
6	0.550	0.497
7	0.625	0.561
8	0.725	0.633
9	0.821	0.720
10	0.908	0.828
11	0.129	0.117
12	0.166	0.180
13	0.282	0.309
14	0.455	0.439
15	0.547	0.495
16	0.622	0.564
17	0.732	0.643
18	0.828	0.748
19	0.906	0.832

Figure 3

Standardization Curve

for Vapor-Liquid Equilibrium Determination

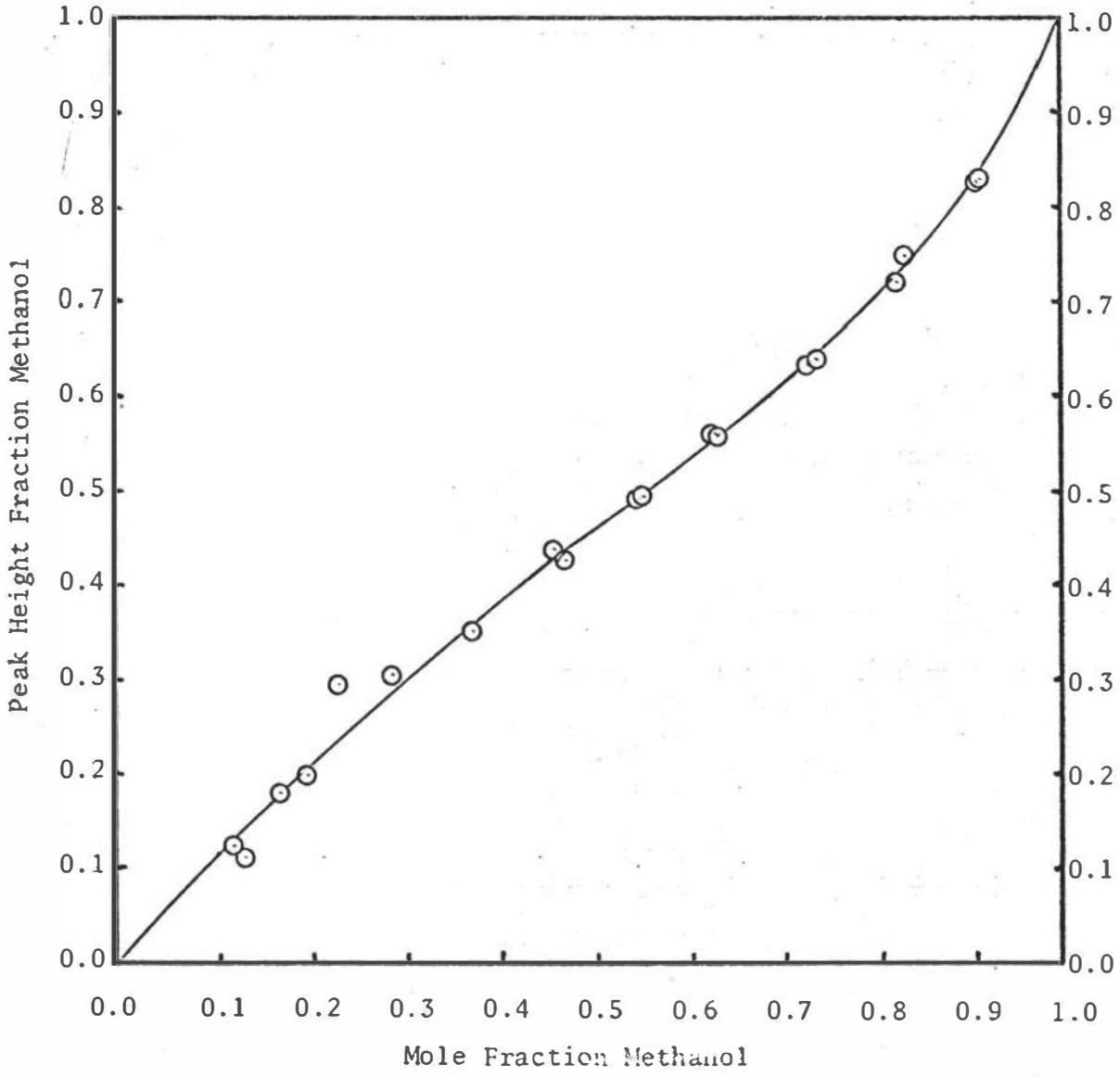


Table 3.

Experimental Vapor Liquid Equilibrium Data for System, Methanol-Cyclohexane.

		Vapor Sample Data			Liquid Sample Data		
Run No.	Temp.* °C	Sample No.	Mole Fraction Methanol	Peak % Methanol	Sample No.	Mole Fraction Methanol	Peak % Methanol
1	62.91	1'	0.919	0.846	1"	0.985	0.981
2	57.48	2'	0.700	0.618	2"	0.955	0.899
3	56.38	3'	0.682	0.604	3"	0.960	0.914
4	55.43	4'	0.654	0.578	4"	0.903	0.823
5	54.61	5'	0.580	0.520	5"	0.827	0.735
6	54.44	6'	0.623	0.555	6"	0.775	0.683
7	54.28	7'	0.600	0.536	7"	0.715	0.631
8	54.40	8'	0.595	0.531	8"	0.620	0.551
9	54.35	9'	0.608	0.536	9"	0.500	0.457
10	74.04	10'	0.253	0.248	10"	0.002	0.002
11	57.99	11'	0.555	0.501	11"	0.018	0.018
12	54.64	12'	0.608	0.543	12"	0.090	0.090
13	54.39	13'	0.610	0.543	13"	0.208	0.208
14	54.36	14'	0.606	0.541	14"	0.310	0.302
15	54.29	15'	0.617	0.548	15"	0.507	0.461
16	54.29	16'	0.605	0.540	16"	0.631	0.561
17	54.34	17'	0.614	0.546	17"	0.712	0.624
18	54.39	18'	0.622	0.553	18"	0.781	0.690
19	55.02	19'	0.600	0.535	19"	0.145	0.145
20	58.12	20'	0.570	0.514	20"	0.025	0.025
21	61.02	21'	0.506	0.464	21"	0.010	0.010
22	67.62	22'	0.413	0.394	22"	0.005	0.005
23	75.52	23'	0.168	0.168	23"	0.000	0.000
24	62.13	24'	0.881	0.796	24"	0.995	0.974
25	60.43	25'	0.812	0.716	25"	0.987	0.962
26	59.03	26'	0.762	0.671	26"	0.975	0.940
27	57.13	27'	0.687	0.606	27"	0.957	0.901
28	55.63	28'	0.647	0.575	28"	0.920	0.845

* Temperature adjusted to 760 torr.

Boiling Point Methanol: 64.94 degrees C.

Boiling Point Cyclohexane: 80.83 degrees C.

Figure 4

Boiling Point Diagram (Mole Fraction vs. Temperature)

for the System Methanol-Cyclohexane

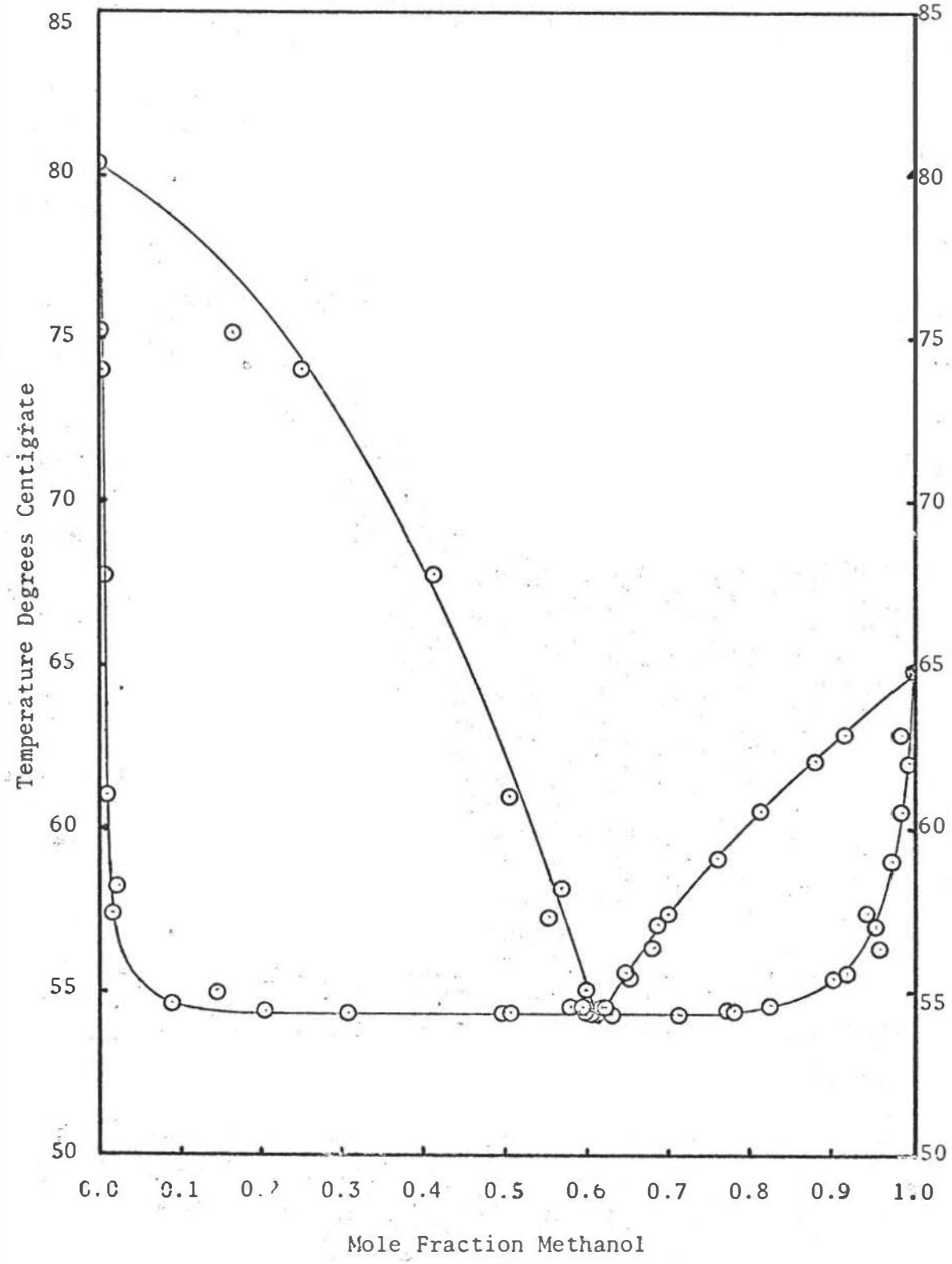


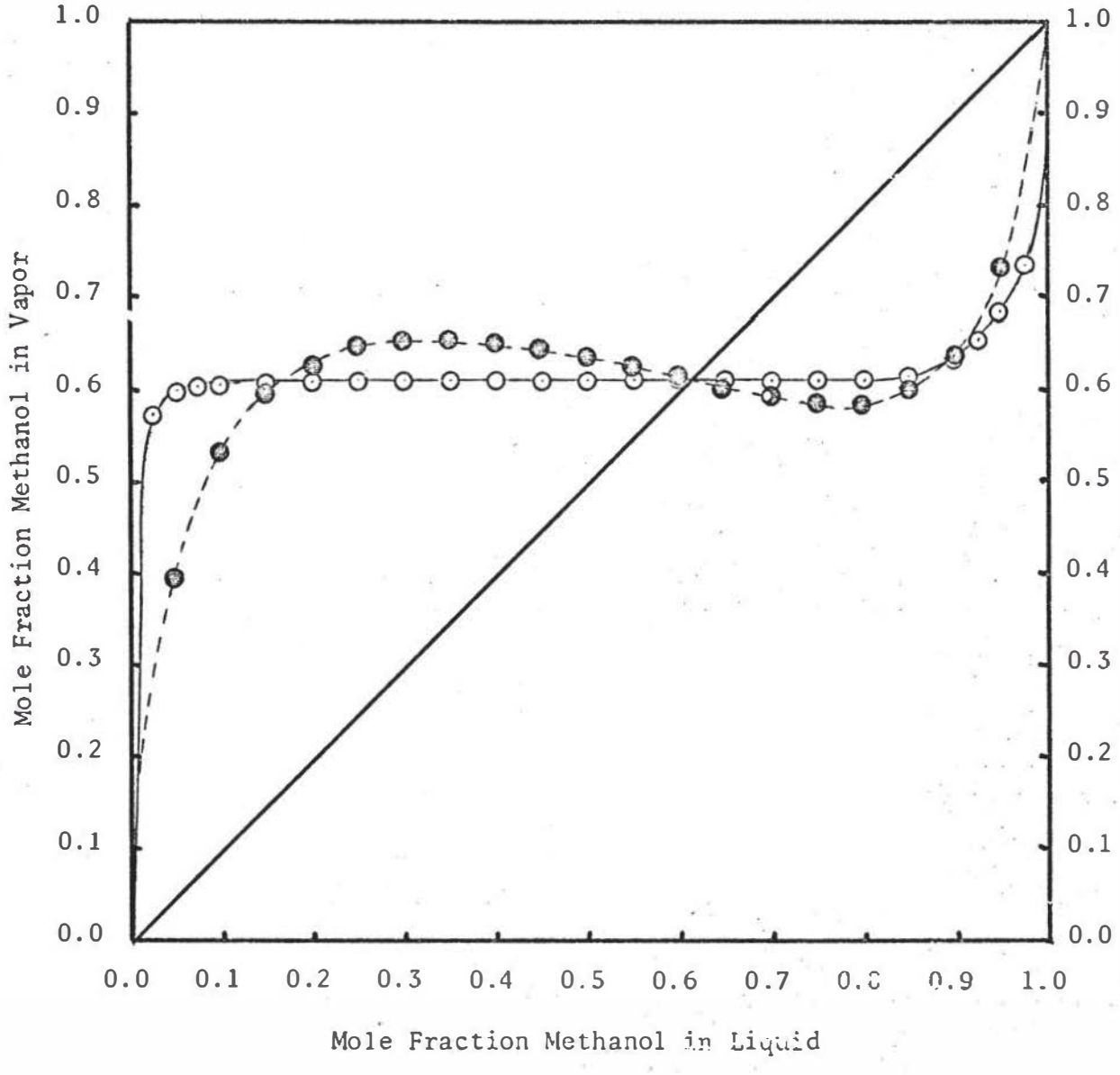
Table 4.

Data for Distillation Curve for System, Methanol-Cyclohexane.

Experimental		Theoretical (van Laar)	
Mole % Methanol in Liquid	Mole % Methanol in Vapor	Mole % Methanol in Liquid	Mole % Methanol in Vapor
0.025	0.575	0.050	0.396
0.050	0.600	0.100	0.532
0.075	0.603	0.150	0.595
0.100	0.606	0.200	0.629
0.150	0.608	0.250	0.646
0.200	0.610	0.300	0.654
0.250	0.610	0.350	0.655
0.300	0.610	0.400	0.651
0.350	0.610	0.450	0.644
0.400	0.610	0.500	0.635
0.450	0.610	0.550	0.628
0.500	0.610	0.600	0.612
0.550	0.610	0.650	0.601
0.600	0.610	0.700	0.591
0.650	0.610	0.750	0.586
0.700	0.610	0.800	0.587
0.750	0.610	0.850	0.600
0.800	0.610	0.900	0.639
0.850	0.617	0.950	0.733
0.900	0.633		
0.925	0.655		
0.950	0.685		
0.975	0.735		

Figure 5

Distillation Curve for System Methanol-Cyclohexane



THEORETICAL

Measurements of the boiling temperatures of solutions of similar mole fractions were made on separate days during which the barometric pressures were 753.2 torr. and 738.3 torr. These data permitted a $\Delta T/\Delta P$ constant to be determined; and safely assuming that a straight line relationship holds in the region between 740-760 torr., all boiling temperatures were adjusted corresponding to a pressure of 760 torr. The boiling point diagram for this adjusted data permitted the calculation of activity coefficients (γ). At equilibrium the partial molal free energy or chemical potential (μ) of the vapor is equal to that of the liquid. From free energy principles $\mu = \mu^\circ + RT \ln a$, where a is the activity and μ° is the chemical potential in the standard state for a given component. The vapors usually show reasonable agreement with the ideal gas law up to a pressure of one atmosphere in which case $\mu = \mu^\circ + RT \ln P/P^\circ$,[9] where P is the partial vapor pressure for one component at a specified temperature and P° is the vapor pressure of that pure component at the same temperature. From Dalton's Law, $P = P_{tot}\ Y$, where P_{tot} is the atmospheric pressure and Y is the mole fraction of the component in the vapor. P° is calculated from Antoine's vapor pressure data taken from Lange.[8] It is evident that $a = P/P^\circ$, which permits activity coefficient

measurements to be made from the relationship $\gamma = a/x$, where x is the mole fraction of the component in the liquid.

The experimentally determined activity coefficients were compared to theoretical activity coefficients as calculated from the equations of Scatchard-Hamer, Margules and van Laar. These equations are derived from excess free energy considerations:[5]

In non-ideal solution: $\mu_i = \mu_i^\circ + RT \ln x + RT \ln \gamma_i$, the $RT \ln \gamma_i$ term $= \partial G^\varepsilon / \partial n_i$, where G^ε is the excess free energy.

It was pointed out by Wohl that excess free energy can be expressed empirically, considering the interactions between molecules, two and three at a time for a binary system as:

$$\frac{G^\varepsilon}{RT\ (q_1x_1 + q_2x_2)} = z_1z_2\ 2a_{12} + z_1^2z_2\ 3a_{112} + z_1z_2^2\ 3a_{122},$$

where a_{12}, a_{122}, and a_{112} are empirical constants, x_1 = mole fraction of component 1, q = effective molar volume of component 1, and z_1 = effective volume fraction of component 1 = $\frac{x_1q_1}{x_1q_1 + x_2q_2}$, where $x_1 + x_2 = 1.0$ and $z_1 + z_2 = 1.0$.

On rearrangement:

$$\frac{G^\varepsilon}{RT} = \left[x_1 + (q_2/q_1)\ x_2\right]\ z_1z_2\ \left[z_1q_1(2a_{12} + 3a_{112}) + z_2q_1\ (2a_{12} + 3a_{112})\right]$$

Substituting: $A' = q_1\ (2a_{12} + 3a_{122})$, $B' = q_2\ (2a_{12} + 3a_{112})$,

$$\frac{G^\varepsilon}{RT} = \left[x_1 + (q_2/q_1)\ x_2\right]\ z_1z_2\ \left[z_1\ (q_1/q_2)\ B' + z_2\ A'\right],$$

which further reduces to:

$$\frac{G^E}{RT} = \frac{n_1^2 n_2 B' + n_1 n_2^2 (q_2/q_1)^2 A'}{\left(n_1 + (q_2/q_1)\, n_2\right)^2} .$$

Upon differentiation with respect to n_1, where $A = 2.303\ A'$ and $B = 2.303\ B'$:

$$\frac{G^E}{2.303 \partial n_1 RT} = \log \gamma_1 = \frac{n_2^2 (q_2/q_1)^2 \left[-n_1 A + 2n_1 B(q_1/q_2) + n_2 A(q_2/q_1)\right]}{\left(n_1 + n_2 (q_2/q_1)\right)^3} .$$

Re-introducing z_1 and z_2:

$$\log \gamma_1 = z_2^2 \left\{A + 2\left[B(q_1/q_2) - A\right] z_1\right\}$$

$$\log \gamma_2 = z_1^2 \left\{B - 2\left[A(q_2/q_1) - B\right] z_2\right\} ,$$

where A, B, and q_1/q_2, are three empirical constants.

If V_1/V_2 is substituted for q_1/q_2, the above results in the Scatchard-Hamer equations. If 1 is substituted for q_1/q_2, the above results in the Margules equation. If A/B is substituted for q_1/q_2, the above results in the van Laar equation, which simplifies to the following form:

$$\log \gamma_1 = \frac{A x_2^2}{\left[(A/B)x_1 + x_2\right]^2}$$

$$\log \gamma_2 = \frac{B x_1^2}{\left[x_1 + (B/A)x_2\right]^2} .$$

From the previous relationship, $\gamma_1 = \frac{P_{tot}\, Y}{P^\circ\ X}$. If measured at the azeotrope, $X = Y$, therefore $\gamma_1 = \frac{P_{tot}}{P^\circ}$ (for the azeotrope only).

This measurement permits the parameters of A and B of the above equations to be determined. From these parameters, an entire set of theoretically predicted activity coefficients may be determined over the entire concentration range. The van Laar constants for the system cyclohexane and methanol were determined to be A = 0.9854 and B = 1.1712.

The thermodynamic consistency of the experimental measurements can be evaluated by the application of the Gibbs-Duhem equation:

$$\frac{d \log \gamma_1}{dx} = -\left[\frac{1-x}{x}\right]\left[\frac{d \log \gamma_2}{dx}\right] .$$

The equation is applicable rigorously only to isothermal data but may be used with the data of the present experiment without serious error due to the small temperature range involved.[9]

Table 5.

Activity Coefficients for Methanol and Cyclohexane.

Experimental			van Laar		
Mole Fraction Methanol	γ_1	γ_2	Mole Fraction Methanol	γ_1	γ_2
0.025	31.000	0.936	0.000	9.669	1.000
0.050	17.140	0.968	0.050	8.009	1.005
0.075	11.760	0.999	0.100	6.670	1.020
0.100	9.044	1.029	0.150	5.586	1.046
0.150	6.146	1.095	0.200	4.706	1.085
0.200	4.655	1.164	0.250	3.990	1.138
0.250	3.724	1.242	0.300	3.406	1.209
0.300	3.104	1.331	0.350	2.929	1.300
0.350	2.660	1.433	0.400	2.538	1.417
0.400	2.328	1.553	0.450	2.217	1.566
0.450	2.069	1.694	0.500	1.953	1.756
0.500	1.862	1.863	0.550	1.736	1.999
0.550	1.693	2.070	0.600	1.559	2.315
0.600	1.552	2.329	0.650	1.413	2.726
0.650	1.433	2.661	0.700	1.295	3.266
0.700	1.330	3.105	0.750	1.200	3.989
0.750	1.241	3.726	0.800	1.126	4.967
0.800	1.164	4.658	0.850	1.071	6.314
0.850	1.104	5.887	0.900	1.031	8.201
0.900	1.041	8.296	0.950	1.008	10.898
0.925	1.023	10.390	1.000	1.000	14.832
0.950	0.996	13.990			
0.975	0.971	21.880			

Figure 6

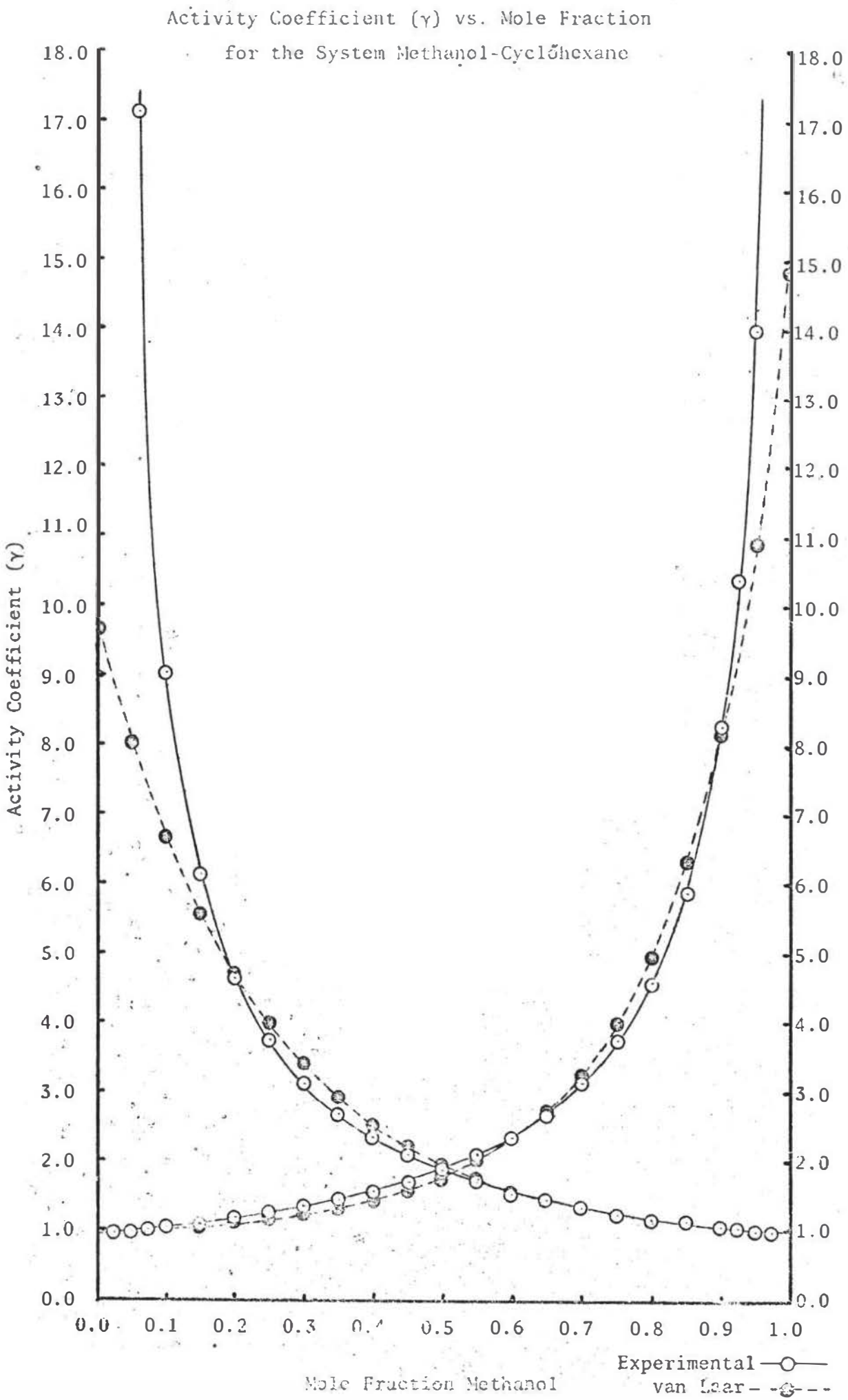

Activity Coefficient (γ) vs. Mole Fraction
for the System Methanol-Cyclohexane
Activity Coefficient (γ)
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Mole Fraction Methanol
Experimental
van Laar

Figure 7

Gibbs-Duhem Application to Experimental Data

for System Methanol-Cyclohexane

(Over a concentration range of 0.10 to 0.90 mole fraction Methanol)

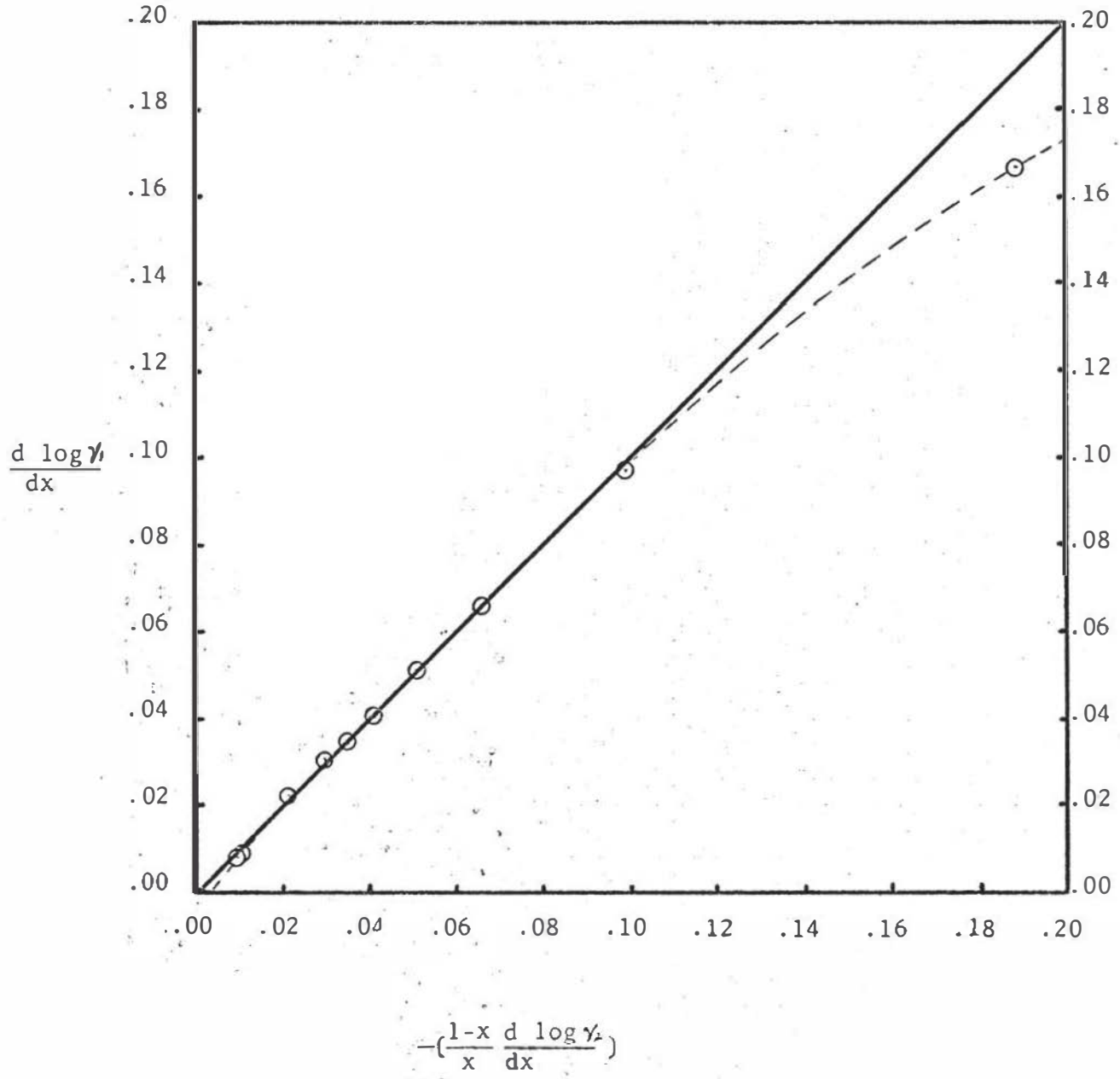
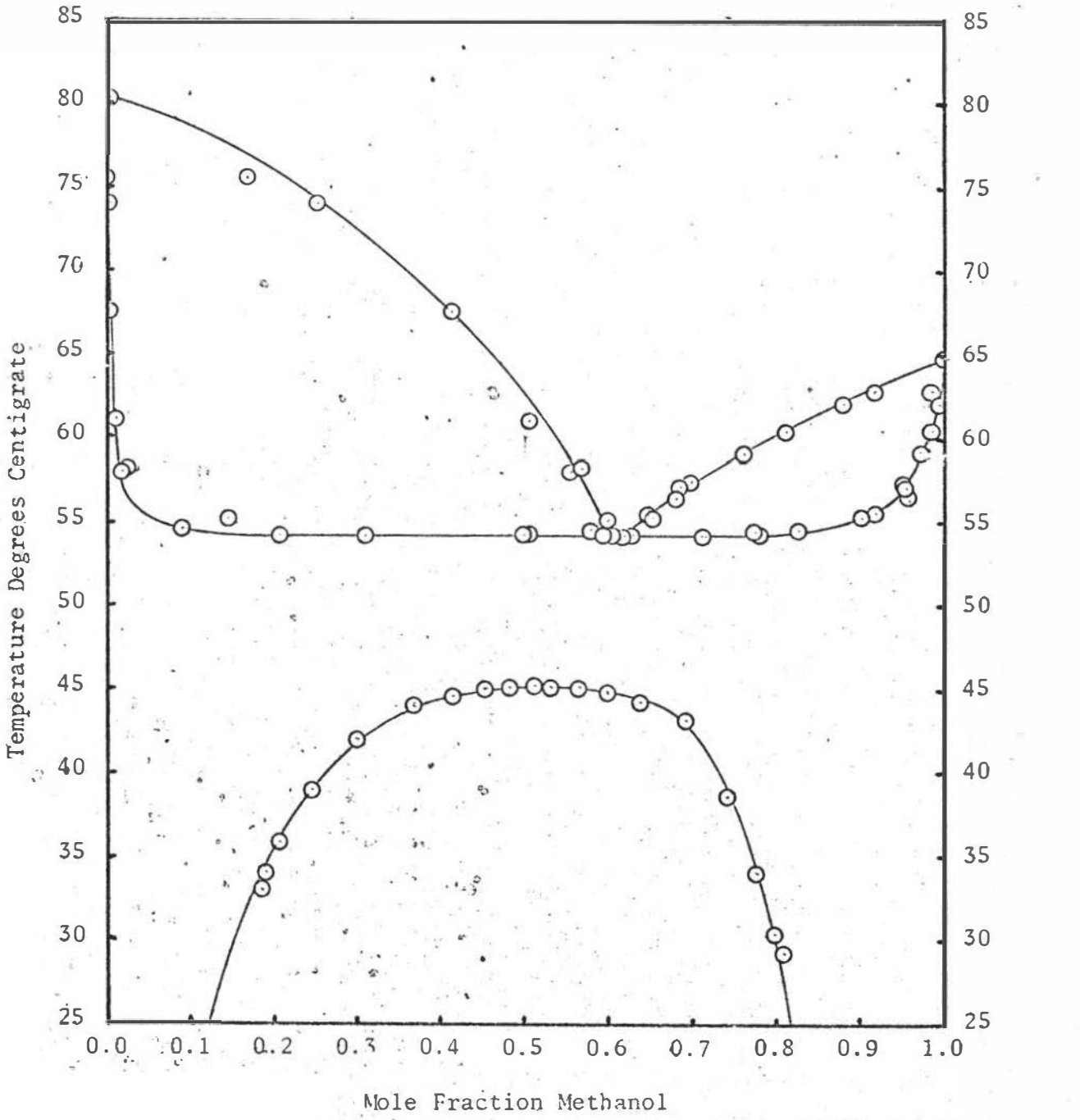


Figure.8

Temperature vs. Mole Fraction for System Methanol-Cyclohexane

(Combined Liquid-Liquid & Vapor-Liquid Equilibrium)



(Liquid-Liquid Phase Data from Eckfeldt - 1943)

DISCUSSION

The data for the mutual miscibility diagram of the system under investigation was found to lie everywhere above the curve determined by Eckfeldt and Lucasse. This discrepancy is probably caused by water impurity in the components of the present experiment. "0.01 percent of water in the alcohol produces a rise of 0.15 degrees C."[7] as measured at the critical solution temperature. In addition, other impurities such as acetone presented a problem in the purification of methanol.[1] Cyclohexane is also difficult to obtain in a completely anhydrous state.[3] The extensive efforts made to dry both components by Eckfeldt and Lucasse were not carried out in the present experiment since time did not warrant the measure, and the sophistication of the apparatus used could not merit such purity.

The effect of pressure on the system was reported to be +0.0314 degrees C. per kilogram per square centimeter.[10] The difference between atmospheric pressure and pressure within the ampoule would not appreciably affect the accuracy of the measurement of the system.

The Choppin-Cottrell circulation still used in the present investigation incorporated in its design several of

the requirements of stills which are used exclusively for measurements of partially miscible systems. One of these features is the design of the receiver of the Choppin-Cottrell still. It functions in approximately the same manner as does the receiver of the still used by T. E. Smith and R. F. Bonner[9] in that the condensate returns directly to the boiling flask from the bottom of the receiver. This helps prevent the condensate from separating into two layers thus returning to the boiling flask in an improper ratio, as is often the case with receivers which empty from above. A second aspect of the Choppin-Cottrell still is that the receiver is mounted close enough to the boiling flask to remain hot enough so that the condensate temperature does not fall below that of mutual miscibility. The Thornton still accomplishes the same end by mounting the receiver within the boiling flask.[4]

The vapor-liquid equilibrium diagram yielded activity coefficients which were unusually high in the more dilute regions. Hydrogen-bonding of the methanol accounts for most of this behavior. In dilute solutions of methanol where the alcohol molecules are too far apart for effective hydrogen bonding, the smaller alcohol molecules acquire a greater chemical potential and consequently a higher activity coefficient. When the concentration of alcohol is high, the strong forces of hydrogen bonding "squeeze" the nonpolar, unhydrogen-bonded cyclohexane molecules out of

solution.[11]

The theoretical activity coefficients as calculated using the Scatchard-Hamer equations showed great deviation from experimental results, especially for the activity coefficients of cyclohexane. This discrepancy is due to the sizable difference in the actual molal volumes of the two components. This difference introduces greater error since these molal volumes are expressed as ratios. The activity coefficients calculated from the Margules equations agreed closely with those derived from experimental data, since unity was substituted for the volume ratios. The van Laar equations also eliminated deviations from marked volume differences by substituting the ratio of the constants for the volume ratio.

The van Laar and Margules equations gave nearly identical data since the constant ratio used in the van Laar equations approximates unity.

The experimental activity coefficients demonstrated reasonable agreement with the application of the Gibbs-Duhem equation. The deviation in the region from 0.14 to 0.20 is indicative of behavior in the low concentration range of methanol since the scale on the abscissa is not related linearly to the mole fraction.

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